

P1 1154225

REC'D 21 APR 2004

WIPD PGT

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office

April 15, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/440,902

FILING DATE: January 17, 2003

RELATED PCT APPLICATION NUMBER: PCT/US04/01575

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS



T. Wallace
T. WALLACE
Certifying Officer

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

01-21-03 150440902-011703 *APR*

01/17/03

150440902 U.S. PTO

PROVISIONAL APPLICATION COVER SHEET [37 CFR 1.53(c)]

This is a request for filing a PROVISIONAL APPLICATION under 35 U.S.C. §111(b) and 37 CFR 1.51(a)(3)

Date : January 17, 2003

Docket No. : 49622/JWP/L471

EXPRESS MAIL NO. EL818363166US

Mail to: **BOX PROVISIONAL PATENT APPLICATION**

150440902 U.S. PTO
60/440902

INVENTOR(S)/APPLICANT(S) (LAST NAME, FIRST NAME, MIDDLE INITIAL, RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY))

SCHROERS, Jan - Pasadena, California

JOHNSON, William L. - Pasadena, California

TITLE OF THE INVENTION (280 characters max)

METHOD OF MANUFACTURING AMORPHOUS METALLIC FOAM

APPLICANT(S) STATUS UNDER 37 CFR § 1.27

☒ Applicant(s) and any others associated with it/them under § 1.27(a) are a SMALL ENTITY

ENCLOSED APPLICATION PARTS

20 Specification (number of pages)

10 Drawings (number of sheets)

☐ Assignment

☒ Other (specify): Title Cover Page

FEE AND METHOD OF PAYMENT

☒ A check for the filing fee of \$ 80.00 is enclosed.

The Commissioner is hereby authorized to charge any fees under 37 CFR 1.16 and 1.17 which may be required by this filing to Deposit Account No. 03-1728. Please show our docket number with any charge or credit to our Deposit Account. **A copy of this letter is enclosed.**

☐ No filing fee enclosed.

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No ☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Please address all correspondence to **CHRISTIE, PARKER & HALE, LLP, P.O. Box 7068, Pasadena, CA 91109-7068, U.S.A.**

Respectfully submitted,

CHRISTIE, PARKER & HALE, LLP

By

John W. Peck
John W. Peck, Ph.D.
Reg. No. 44,284
626/795-9900

JWP/syb

PROVISIONAL APPLICATION FILING ONLY



23363

PATENT TRADEMARK OFFICE

PROVISIONAL PATENT APPLICATION

of

Jan Schroers
and
William L. Johnson

for

**METHOD OF MANUFACTURING
AMORPHOUS METALLIC FOAM**

Attorneys
CHRISTIE, PARKER & HALE, LLP
P.O. Box 7068
Pasadena, CA 91109-7068

Docket No. 49622/JWP/L471

*This paper or fee is being deposited with the
U.S. Postal Service "Express Mail Post Office to
Addressee" under 37 CFR 1.10, Mailing Label
No. EL818363166US.*

METHOD OF MANUFACTURING AMORPHOUS METALLIC FOAM

FIELD OF THE INVENTION

The present invention is directed to novel methods of manufacturing amorphous metallic foams; and more particularly to amorphous metallic foams made from bulk-solidifying amorphous alloys.

BACKGROUND OF THE INVENTION

Metallic foams are known to have interesting combinations of physical properties. They offer high stiffness in conjunction with very low specific weight, high gas permeability, and a very high energy absorption ability. Today, these materials are emerging as a new engineering material. Foams can be classified as either open or closed porous. Whereas open foams are mainly used as functional materials such as gas permeability membranes, closed foams find application as structural materials such as energy absorbers or light-weight stiff materials. However, the broad-use of metallic foams is hindered by the ability to produce uniform and consistent foam structures. Specifically, prior manufacturing methods for producing metallic foams result in an undesirably wide distribution of cell and/or pore sizes which cannot be controlled satisfactorily, and as such limits and degrades the functional and structural characteristics of the metallic foam materials.

The production of metallic foamed structures is generally carried out in the liquid state above the melting temperature of the material, though some solid-state methods have also been used. The foaming of ordinary metals is challenging because a foam is an inherently unstable structure. The reason for the imperfect properties of conventional metallic foams comes from the manufacturing process itself. For example, although a pure metal or metal alloy typically consists of a large volume fraction ($>50\%$) of gas bubbles, manufacturing metallic foam from ordinary alloys is very difficult because a desired bubble distribution can not be readily sustained for practical times in their molten state.

Specifically, the time scales for the flotation of bubbles in a foam scales with the viscosity of the material. Accordingly, the mechanical properties of these foams

drastically degrade with the degree of imperfection caused by the flotation and bursting of bubbles during manufacture. In addition, the low viscosity of the commonly used liquid metals results in a short time scale which makes the processing of metallic foam a delicate process.

In order to remedy these shortcomings, several other techniques have been attempted. For example, to reduce the sedimentation flotation process, Ca particles may be added to the liquid, however, the addition of Ca itself degrades the metallic nature of base metal itself as well as the metallic foam. Alternatively, foaming experiments have been performed under reduced gravity, in space, to reduce the driving force for flotation, however, the cost for manufacturing metallic foams in space is prohibitive.

It appears that none of the remedies utilized in the manufacturing of ordinary metallic foams are satisfactorily adequate for the production of amorphous metallic foam materials. Accordingly, a need exists for improved methods for manufacturing amorphous metallic foams which also can be used for the production of better-controlled foam structures.

SUMMARY OF THE INVENTION

The present invention describes a method of controllably manufacturing amorphous metallic foams from amorphous alloys, and more particularly to controllably manufacturing metallic foams from bulk solidifying amorphous alloys.

In another embodiment of the invention, the volume fraction of bubbles in the metallic foam can be continuously varied between $>1\%$ and $\sim 95\%$. In such an embodiment, the bubble size can also be continuously varied between $\sim 2 \mu\text{m}$ and $\sim 4 \text{mm}$ average size.

In still another embodiment of the invention, the amorphous alloy is a bulk-solidifying amorphous alloy, where it is defined as an alloy that can be cast with a dimension of more than 1 mm in its smallest dimension.

In yet another embodiment, the invention is directed to a method of making amorphous metallic foams comprising the steps of:

- a. Making a "pre-cursor" by introducing gas bubbles (volume fraction $< 30\%$) with an average size less than 1 mm (average by number and not by volume

fraction) to the liquid metal at a temperature above the liquidus temperature of the alloy, where the processing pressure is high (up to 50 bars) to create a high pressure in the bubbles.

b. Cooling the bubble consisting liquid such that it maintains its amorphous state.

c. Subsequent expansion of the pre-cursor under a pressure gradient at a temperature where the viscosity is between 10^{12} Pa s and 10^5 Pa s. In such an embodiment, in order to establish a pressure gradient the pressure applied during step c must be lower than the pressure during step a.

In still yet another embodiment of the invention, the cooling step of the method entails fully solidifying the pre-cursor. In such an embodiment, the solidified precursor must be reheated to around the supercooled region in the subsequent expansion step.

In still yet another embodiment of the invention, the gas bubbles are introduced to the liquid by stirring the liquid which distributes bubbles through the liquid surface.

In still yet another embodiment of the invention, the gas is introduced to the liquid through a nozzle.

In still yet another embodiment of the invention, the stirring of the liquid is used to chop off existing liquids to obtain smaller bubbles.

In still yet another embodiment of the invention, the gas bubbles are introduced to the liquid by adding an agent that releases gas at this temperatures and therefore leads to the creation of bubbles.

In still yet another embodiment of the invention, the method includes the step of introducing a volume fraction of $< 30\%$ of small bubbles (between $1\text{ }\mu\text{m}$ and 1 mm) to molten alloy liquid at or above the liquidus temperature. In such an embodiment, the bubble containing liquid is solidified and its amorphous structure is maintained to produce a foam "pre-cursor". In such an embodiment, the foam pre-cursor is preferably an amorphous metal alloy consisting of up to 30% bubbles with a size distribution between $1\text{ }\mu\text{m}$ and 1 mm .

In still yet another embodiment the invention is directed to a method of forming articles of amorphous metallic foams having a very narrow distribution of bubble sizes. In such an embodiment the bubbles may have a size distribution of a few μm , for example, between about 1 and $10\text{ }\mu\text{m}$.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features and advantages of the present invention will be better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings wherein:

Figure 1 is a graphical representation of the time, temperature and transformation (TTT diagram) properties of an embodiment ($Zr_{58.5}Nb_{2.8}Cu_{15.6}Ni_{12.8}Al_{10.3}$ (% atom.) called VIT-106a) of a suitable materials for manufacturing amorphous metallic foams according to the current invention.

Figure 2 is a graphical representation of the viscosity properties of an embodiment (Zr-Ti-Ni-Cu-Be VIT-1 series) of a suitable materials for manufacturing amorphous metallic foams according to the current invention.

Figure 3a is a flowchart of a first embodiment of a method of manufacturing amorphous metallic foams according to the current invention.

Figure 3b is a flowchart of a second embodiment of a method of manufacturing amorphous metallic foams according to the current invention.

Figure 4a is a graphical representation of the flotation properties of an embodiment ($Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ (% atom.) called VIT-1) of a suitable materials for manufacturing amorphous metallic foams according to the current invention

Figure 4b is a graphical representation of the flotation properties of an embodiment ($Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ (% atom.) called VIT-1) of a suitable materials for manufacturing amorphous metallic foams according to the current invention as compared to pure Al metal..

Figure 5a is a pictorial representation of an embodiment of a foam precursor manufactured according to the current invention.

Figure 5b is a pictorial representation of an embodiment of a foam precursor ~~manufactured~~ manufactured according to the current invention.

Figure 6 is a schematic of an embodiment of an apparatus for manufacturing metallic foams according to the current invention.

Figure 7 is a pictorial representation of an embodiment of a foam precursor ($\text{Zr}_{58.5}\text{Nb}_{2.8}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}$ (% atom.) called VIT-106a) manufactured according to the current invention.

Figure 8 is a graphical representation of the properties of an embodiment ($\text{Zr}_{58.5}\text{Nb}_{2.8}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}$ (% atom.) called VIT-106a) of a suitable materials for manufacturing metallic foams according to the current invention.

Figure 9 is a graphical representation of the properties of an embodiment ($\text{Zr}_{58.5}\text{Nb}_{2.8}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}$ (% atom.) called VIT-106a) of a suitable materials for manufacturing metallic foams according to the current invention.

Figure 10 is a pictorial representation of an embodiment of an amorphous metallic foam manufactured according to the current invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a method of controllably manufacturing amorphous metallic foams from amorphous alloys and more particularly from bulk-solidifying amorphous alloys.

Bulk solidifying amorphous alloys are amorphous alloys, which can be cooled at substantially lower cooling rates, of about 500 K/sec or less, and retain their amorphous atomic structure substantially. As such, they can be produced in thickness of 1.0 mm or more, substantially thicker than conventional amorphous alloys of typically 0.020 mm which require cooling rates of 10^5 K/sec or more. Furthermore, bulk-solidifying-amorphous alloys generally show a distinct glass transition before crystallization upon heating from the ambient temperatures. Bulk-solidifying amorphous alloys generally show a ΔT (defined below) of larger than 30 °C. U.S. Patent Nos. 5,288,344; 5,368,659; 5,618,359; and 5,735,975 (the disclosure of each of which is incorporated herein by reference in its entirety) disclose such bulk solidifying amorphous alloys. A family of bulk solidifying amorphous alloys can be described as $(\text{Zr},\text{Ti})_a(\text{Ni},\text{Cu},\text{Fe})_b(\text{Be},\text{Al},\text{Si},\text{B})_c$, where a is in the range of from 30 to 75, b is in the range of from 5 to 60, and c in the range of from 0 to 50 in atomic percentages. Furthermore, those alloys can accommodate substantial amounts of other transition metals up to 20 % atomic, and more preferably

49622/JWP/L471

metals such as Nb, Cr, V, Co. A preferable alloy family is $(\text{Zr,Ti})_a(\text{Ni,Cu})_b(\text{Be})_c$, where a is in the range of from 40 to 75, b is in the range of from 5 to 50, and c in the range of from 5 to 50 in atomic percentages. Still, a more preferable composition is $(\text{Zr,Ti})_a(\text{Ni,Cu})_b(\text{Be})_c$, where a is in the range of from 45 to 65, b is in the range of from 7.5 to 35, and c in the range of from 10 to 37.5 in atomic percentages. Another preferable alloy family is $(\text{Zr})_a(\text{Nb,Ti})_b(\text{Ni,Cu})_c(\text{Al})_d$, where a is in the range of from 45 to 65, b is in the range of from 0 to 10, c is in the range of from 20 to 40 and d in the range of from 7.5 to 15 in atomic percentages.

Another set of bulk-solidifying amorphous alloys are ferrous metals (Fe, Ni, Co) based compositions. Examples of such compositions are disclosed in U.S. Patent No. 6,325,868, (A. Inoue et. al., Appl. Phys. Lett., Volume 71, p 464 (1997)), (Shen et. al., Mater. Trans., JIM, Volume 42, p 2136 (2001)), and Japanese patent application 2000126277 (Publ. # .2001303218 A), all of which are incorporated herein by reference. One exemplary composition of such alloys is $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$. Another exemplary composition of such alloys is $\text{Fe}_{72}\text{Al}_7\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$. Although, these alloy compositions are not as processable to the degree of Zr-base alloy systems, they can be still be processed in thicknesses around 1.0 mm or more, sufficient enough to be utilized in the current invention.

Although any of the above bulk-solidifying amorphous alloys may be utilized, in one preferred embodiment the bulk-solidifying amorphous alloy has a ΔT of larger than 60 °C and preferably larger than 90 °C. ΔT defines the extent of supercooled liquid regime above the glass transition temperature, to which the amorphous alloy can be heated without significant crystallization in a typical Differential Scanning Calorimetry experiment.

In general, crystalline precipitates in amorphous alloys are highly detrimental to their properties, especially to the toughness and strength, and as such it is generally preferred to limit these precipitates to as small a minimum volume fraction possible so that the alloy is substantially amorphous. However, there are cases in which, ductile crystalline phases precipitate in-situ during the processing of bulk amorphous alloys, which are indeed beneficial to the properties of bulk amorphous alloys especially to the toughness and ductility. The volume fraction of such beneficial (or non-detrimental)

crystalline precipitates in the amorphous alloys can be substantial. Such bulk amorphous alloys comprising such beneficial precipitates are also included in the current invention. One exemplary case is disclosed in (C.C. Hays et. al, Physical Review Letters, Vol. 84, p 2901, 2000), the disclosure of which is incorporated herein by reference. For the purposes of this invention, the term amorphous means at least 50% by volume of the alloy is in amorphous atomic structure, and preferably at least 90% by volume of the alloy is in amorphous atomic structure, and most preferably at least 99% by volume of the alloy is in amorphous atomic structure.

Although bulk-solidifying amorphous alloys are discussed above, it should be understood that any suitable amorphous alloy, especially ones with a ΔT of larger than 30 °C, may be used in the current invention.

The amorphous alloys and specifically bulk-solidifying amorphous alloys are characterized by relatively sluggish crystallization kinetics. The sluggish crystallization kinetic makes the whole or a portion of the under cooled liquid region, the temperature region between the liquidus temperature and the glass transition temperature, accessible for practical times, as shown in Figure 1. For example, the time before crystallization sets in was experimentally determined, in an isothermal experiment, for the whole under cooled liquid region and is summarized in time temperature transformation (TTT) diagrams for a few of amorphous alloys ($Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$, $Zr_{58.5}Nb_{2.8}Cu_{15.6}Ni_{12.8}Al_{10.3}$, $Pd_{43}Ni_{10}Cu_{27}P_{20}$). Figure 1 shows the TTT-diagram for $Zr_{58.5}Nb_{2.8}Cu_{15.6}Ni_{12.8}Al_{10.3}$ (VIT-106a).

The undercooled region is accessed by cooling from the stable liquid (circles) and by heating the solid amorphous state (squares). At low temperatures, below 750 K, no noticeable difference between the heated and cooled samples in the undercooled liquid can be observed provided that such heating and cooling is achieved sufficiently fast to avoid any significant crystallization.

Furthermore, a relatively large range of viscosity values can be observed in the undercooled liquid regime of bulk-solidifying amorphous alloys. For example, Figure 2 shows the viscosity as a function of temperature for $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ (VIT-1) As shown, the viscosity of this bulk-solidifying amorphous alloy changes by ~13 orders of magnitude in the undercooled liquid regime.

The applicants discovered that the sluggish crystallization kinetics (see Figure 1) can be beneficially exploited to develop novel processing methods of bulk-solidifying amorphous alloys into foam structures. Furthermore, the applicants discovered that utilizing these novel processing methods and by accessing a large regime of viscosity values, between ~ 1 Pa s and $\sim 10^{13}$ Pa s, highly homogeneous and controllable amorphous metallic foam structures can be obtained. The applicants further discovered that, these novel methods of processing amorphous alloys into metallic foam structures can substantially forego or relax the dimensional limitations arising from critical cooling rate to form amorphous phase.

The processing method, according to the present invention, for making foams from bulk-solidifying amorphous alloy exhibiting a glass transition before crystallization comprises three general steps: 1) creation of a foam pre-cursor; 2) cooling the precursor; and 3) expanding the bubbles in the precursor to form a final metallic foam. Flow charts of two embodiments of this general process are shown in Figures 3a and 3b. As seen, both methods generally entail the steps as recited below.

First, creating a bulk-solidifying amorphous alloy "pre-cursor" at temperatures above the liquidus temperature of the alloy which consists of a moderate volume fraction ($<30\%$) of small bubbles (<1 mm), and preferably creating a large pressure in the bubbles by processing the pre-cursor at high pressures (up to ~ 50 bar or more).

Second, solidifying the pre-cursor by cooling the molten alloy sufficiently quickly to maintain its amorphous state.

Finally, heating the solidified precursor to allow the bubbles to expand in the supercooled liquid region of the bulk-solidifying amorphous alloy under a pressure gradient by processing the material at lower pressures than in step 1 (preferably in partial or full vacuum). The supercooled temperature region is where the viscosity of the alloy is between $\sim 10^{12}$ Pa s and $\sim 10^6$ Pa s. It should be understood that the processing time can be any length such that the material does not crystallize during expansion or that the process is terminated before crystallization would set in, resulting in an amorphous foam.

In the method summarized in Figure 3a, the pre-cursor is only cooled in the second step to a super-cooled region, shown in the TTT diagram in Figure 1 below the nose of crystallization curve and above the glass transition temperature. Accordingly, in

this embodiment, the expansion of the bubble does not require any reheating of the precursor, but rather controlled cooling of the precursor into specific temperature zones.

Meanwhile, in the method summarized in Figure 3b, the precursor is cooled to a solidifying temperature (below the glass transition temperature) in Step 2, and then reheated in Step 3 to above the glass transition temperature to allow for the expansion of the bubbles. This embodiment is preferred for manufacturing arrangements in which it is advantageous to be able to handle a stable pre-cursor prior to the preparation of the final metallic foam.

The expansion of the bubbles, and hence the precursor, can be carried out in pre-determined constrained geometry in order to achieve near-to-net-shaped foam components. Furthermore, such operation can be carried as a part of the assembly or mechanical joining operation into other materials.

Although the process discussed above is useful for a wide variety of bulk-solidifying amorphous alloys, it should be understood that the precise processing conditions required for any particular bulk-solidifying amorphous alloy will differ. For example, as discussed above, a foam consisting of a liquid metal and gas bubbles is an unstable structure, flotation of the lighter gas bubbles due to gravitational force takes place, leading to a gradient of the bubbles in size and volume. The flotation velocity of a gas bubble in any liquid metal material can be calculated according to the Stoke's law:

$$V_{sed} = 2 a^2 (\rho_l - \rho_g) g / 9 \eta \quad (1)$$

where g is the gravitational acceleration, a is the bubble radius, and ρ_l , ρ_g , are the densities of the liquid and gas, respectively.

An exemplary flotation velocity calculation made according to Equation 1 for VIT-1 is shown in Figures 4a and 4b. As shown in Figure 4a, using experimental viscosity data (as shown in Figure 2) and a liquid VIT-1 density of $\rho = 6.0 \times 10^3 \text{ kg/m}^3$, the flotation velocities of bubbles in a VIT-1 alloy melt as a function of bubble radius is calculated for liquid VIT-1 at 950 K (—), and 1100 K (- - -). Figure 4b shows the flotation for a 1 mm gas bubble in liquid VIT-1 (—) and liquid Al (- - -) as a function of T/T_l .

Using such graphs, acceptable processing conditions, such as time and temperature can be determined. For example, if the duration of a typical manufacturing process is taken to be 60 s and an acceptable flotation distance of ~ 5 mm, processing times and temperatures resulting in a flotation velocity smaller than 10^{-4} m/s would be acceptable. Therefore, in this case an unacceptable bubble gradient can be avoided if the maximum bubble size is less than $630 \mu\text{m}$ if the VIT-1 melt is processed above its liquidus temperature of about 950 K. By processing VIT-1 melts at 660 K, below its crystallization temperature of 675 K, no noticeable flotation takes place even for ~ 1 cm bubbles. On the other hand, these results show that the formation of gradients in Al-melts cannot be suppressed for bubbles larger than $4 \mu\text{m}$. The TTT-diagram for VIT-1 suggests that, for example, at ~ 700 K it takes 1100 s before the sample crystallizes. This time is available for processing the pre-cursor and expanding the bubbles while avoiding significant crystallization. In Figure 2 the viscosity of VIT-1 is depicted. In the temperature region where the undercooled liquid is accessible the viscosity is between 10^{12} Pa s and 10^6 Pa s. For these viscosity values, bubbles of even several cm in size do not show any noticeable gradient on the time scale of the experiment.

As discussed above, in order to prepare the pre-cursor, a gas has to be introduced into the liquid bulk-solidifying amorphous alloy. Any suitable method of introducing bubbles in the liquid bulk-solidifying amorphous alloy sample may be utilized in the current invention. In one exemplary embodiment, gas releasing agents, such as B_2O_3 can be used which are mixed with the metal alloy. The B_2O_3 releases H_2O_3 at elevated temperatures, which in turn forms gas bubbles in the size range of between $\sim 20 \mu\text{m}$ up to ~ 2 mm. As already demonstrated in the calculations, with these size bubbles no observable gradient takes place in the final metallic foam, as shown in Figures 5a and 5b for B_2O_3 in a PdNiCuP alloy. These figures also demonstrate how the volume fraction of the gas bubbles can be varied with the processing time, temperature, and pressure between 3 % Figure 5a and 20% Figure 5b.

Another method to introduce bubbles into a liquid bulk-solidifying amorphous alloy to obtain a pre-cursor foam is by mechanical treating the liquid as shown in pictorial example of VIT-106a in Figure 7. In such an embodiment, the stability of a

liquid surface can be described by comparing the inertial force to the capillary force, according to the ratio:

$$W = \frac{\rho v^2 L}{\sigma} \quad (2)$$

where W is the Weber number, ρ is the density of the liquid, v the velocity of the moving interface, L a typical length for bubble size, and σ the liquid's surface energy. For $W < 1$ the liquid surface becomes unstable and gives rise to mechanically create bubbles in the liquid. This equation makes it possible to calculate the size of bubbles that can be created for a given inertial force and surface energy. For example, an object with a velocity of 10 m/s moving in a liquid with a density of 6.7 g/cm³ and a viscosity of 1 Pa s is able to break-up bubbles with a size down to 1 μ m.

A schematic of an apparatus capable of creating a pre-cursor according to this method is shown in Figure 6. In this embodiment, a heated crucible 10 holds the liquid alloy sample 12 and a spinning whisk 14 is used to breakup existing bubbles 16 and create new bubbles 18 by breaking up the surface 20 of the liquid. A bubbler 22, consisting in this embodiment of a tube through which gas may be passed is used to create the initial bubbles. Initial bubbles can also be created through the surface by a drag of the liquid created by the spinning whisk.

An example of a Vitreloy 106 pre-cursor made in accordance with this mechanical method is shown in Figure 7. The pre-cursor consists of about 10% bubbles. The bubble size is in between 0.020 mm and 1 mm.

Furthermore, it should be noted that there is a minimum bubble size that can be created with the precursor-forming methods. From the energy considerations, it can be derived that the minimum bubble size, which is given by:

$$R_{min} = 2 \sigma / P \quad (3)$$

where σ is the (surface tension) (as in the above Weber equation), and P is the ambient pressure during bubble creation. It should be noted the bubble size in the foam

precursor are preferably as small as possible in order to obtain a better controlled expansion in the subsequent steps. According to the above formula, a high ambient pressure (up to 50 bars or more) is desired during bubble formation in order to create bubbles in smaller diameters.

Furthermore, the invention is directed to achieve a high degree of homogeneity in bubble distribution in the foam precursor (which in itself can be used a metallic foam material). Nonetheless, the very same foam precursor can be formed into a final foam material of lower density (a higher volume fraction of bubbles), and with a high degree of homogeneity in bubble distribution by utilizing the above-mentioned expansion steps for the foam precursor with homogeneous bubble distribution. Accordingly, a first steady-state bubble distribution is achieved with one of the above processes of bubble generation. This is followed by flotation of larger bubbles by keeping the molten alloy above the liquidus. The specific temperature above the liquidus can be selected by the desired bubble size distribution. The higher temperature above the liquidus, the more smaller bubbles will float within a given time. After the larger size bubbles are floated, the molten alloy is homogenized by a controlled mechanical operation without trapping additional bubbles, for example by submerging the whole whisk into the molten alloy. Accordingly, a new bubble distribution can be achieved with a tighter distribution of smaller bubbles. The above-mentioned steps can be repeated several times in order to achieve the desired distribution of bubble size.

Although the viscosity properties of bulk-solidifying amorphous alloys make it possible to controllably create pre-cursors and preventing serious spatial gradient in bubble distribution, in conventional bulk-solidifying amorphous alloy processing techniques it is critical in the subsequent solidification that the temperature of the foam be controlled to ensure that the amorphous structure of the material is maintained. As a result, this requires cooling the foam material at a rate higher than the critical cooling rate, where the critical cooling rate, R_c , is defined as the lowest cooling rate at which significant crystallization of the material can be avoided upon cooling. In turn, R_c is inversely proportional to the critical casting thickness, D_c . An alloy containing bubbles has a smaller critical casting thickness than the same alloy without any bubbles. Accordingly, the influence of the foaming process on the critical casting thickness,

49622/JWP/L471

assuming the foaming process does not cause heterogeneous nucleation, can be estimated through the increase in thermal diffusion length. For example, if $\alpha_g \ll \alpha_l$ (where α is the thermal conductivity of the g (gas), and l (liquid)), $\rho_g \ll \rho_l$, (where ρ is the density), and $c_{p,g} \leq c_{p,l}$ (where c_p is the specific heat), the heat will predominately transfer through the liquid. But this requires an increased diffusion length since the linear path is interrupted. Assuming a dense packing of spherically shaped, uniform bubbles, with a volume fraction of about 75 %, the additional diffusion length can be calculated by comparing the length of going around a bubble with the bubble diameter, resulting in a factor of $\pi/2$. This results in a critical casting thickness for the foam which is 65% of that of the bulk material. Accordingly, amorphous foam containing 75 % bubbles manufactured by this method would be restricted in one dimension to a thickness D_c (bulk) \times 0.65 .

However, in the technique of the present invention the smallest dimension of the foam is not limited to D_c of the bulk materials. Specifically, in the first step in the processing route according to the present invention an amorphous foam "pre-cursor" consisting of a large number of small bubbles (sized between $\sim 10 \mu\text{m}$ and $\sim 1 \text{ mm}$) with a maximum volume fraction of 30 % is formed. The critical casting thickness of the precursor would be about D_c (bulk) \times 0.8 or larger due to the smaller volume fraction of gas than in the above discussed case with 75% bubbles. This precursor will then subsequently be expanded in the super-cooled liquid region. Here, such restrictions of critical casting thickness do not apply anymore. Instead, the dimensions of the final foam is limited by the number and size of the bubbles, the pressure difference in the step.1 and step 3. .

In order to expand the bubbles in the pre-cursor in the super-cooled liquid region, a difference in pressure inside the bubbles and the pressure in the undercooled liquid is mandatory. Therefore, this processing step has to be performed at a lower pressure than that used in Step 1. The expansion time and temperature can be calculated from the growth of a gas bubble in a liquid according to Equation 4, below.

$$\frac{dR}{dt} = \left(\frac{P_B(R) - P - \frac{2\sigma}{R}}{P_B(R) - P - \frac{2\sigma}{R}} \right) \frac{R}{4\eta} \quad (4)$$

where R is the bubble radius, R ; interfacial energy, σ ; viscosity, η ; pressure in the bubble, P_B ; and the pressure outside the bubble, P . Figure 8 shows the expanding bubble radius of VIT-106a ($Zr_{58.5}Nb_{2.8}Cu_{15.6}Ni_{12.8}Al_{10.3}$ % atomic) as a function of time for different temperatures for a pressure of 3 bar in the bubble and 10^{-6} bar in the liquid. The initial bubble radius is 100 μm . Taken from Figure 1 the time to reach crystallization, which is the available time for the foaming process one can calculate the maximum bubble volume fraction for different pre-cursor. This is done for the considered temperatures in Figure 8, namely 700 K, 730 K, 750 K, and 765 K for a bubble pressure of 3 bar and a liquid pressure of 10^{-6} bar for an initial bubble radius of 100 μm . These results are also summarized in Table 1, below. For example, a pre-cursor that consists of 10% bubbles, processed at 750 K for the available time of 110 s, expands to a bubble volume fraction of 47% and maintains its amorphous structure.

Table 1: Bubble Expansion Versus Time				
T [K]	T cryst [s]	5% %bubble	10% %bubble	20% %bubble
700	3700	9	18	33
730	420	15	27	45
750	110	30	47	67
765	85	33	51	70

Figure 9 shows the influence of the bubble pressure on the expansion. The processing temperature is 750 K, the initial bubble radius is 100 μm , and the pressure in the liquid during expansion is 10^{-6} bar. Table 2 shows the expansion of pre-cursors with 5%, 10%, 20% for bubble pressures of 1 bar, 3 bar, 10 bar, and 30 bar. Especially at high

bubble pressure the pre-cursor can be substantially expanded within the time before crystallization sets in.

Table 2: Bubble Expansion Versus Pressure				
T [K]	P [bar]	5% %bubble	10% %bubble	20% %bubble
750	1	13	23	41
750	3	30	47	67
750	10	53	71	85
750	30	77	88	95

EXAMPLE

In one exemplary embodiment, the bulk glass forming alloy $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ was processed into a low-density amorphous metallic foam. In this embodiment, as described in detail below, $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ is mixed with hydrated B_2O_3 which releases gas at elevated temperature and/or low pressure. Very homogeneous foams are achieved, due to the high viscosity of the alloy even at its liquidus temperature. By processing at the liquidus temperature and decreasing the pressure to 10^{-2} mbar, well distributed bubbles expand to foam the material. Foam densities as low as $1.4 \times 10^3 \text{ kg/m}^3$ were obtained, corresponding to a bubble volume fraction of 84 %. The bubble diameter ranges between $2 \times 10^{-4} \text{ m}$ and $1 \times 10^{-3} \text{ m}$. Thermal analysis by differential scanning calorimetry was then used to confirm the amorphous nature of the foam.

Ingot material of a purity ranging from 99% to 99.999% was used. The prefoam material was prepared by mixing the ingots with B_2O_3 powder in quartz tubes, and processing for 1200 s at 1200 K, followed by water quenching. The temperature was measured with K-type thermocouples. Wavelength-dispersive-spectrometer

49622/JWP/L471

measurements were carried out to verify the composition of the samples. Thermal analysis to confirm the amorphous nature of the foam was performed in a Perkin Elmer DSC 7 analyzer.

Hydrated B_2O_3 was utilized to create gas bubbles in the liquid melt. These bubbles expand when the pressure is decreased, resulting in a low density closed cell foam. Differential scanning calorimetry (DSC) measurements were then carried out to confirm the amorphous nature of the foam. A prefoam specimen prepared in the described way consisted of a uniform distribution of bubbles. The bubble volume fraction was about 20% with an average bubble size of 1.5×10^{-4} m.

The prefoam sample was processed for 60 s at 1100 K to improve the glass forming ability of the material, and subsequently cooled to the alloy's liquidus temperature of about 860 K. Subsequently, the pressure was slowly decreased to about 10^{-2} mbar. The lowering of the pressure results in the foaming of the material. After 20 s, when the material reaches its maximum foam height, it was water quenched. The density of the foam produced was 2.2×10^3 kg/m³ compared to 9.1×10^3 kg/m³ for bulk $Pd_{43}Ni_{10}Cu_{27}P_{20}$ sample. The bubbles in the produced foam vary in diameter between 10^{-4} m and 10^{-3} m. A very uniform bubble distribution can be observed without noticeable gradient from top to bottom.

Using previously published viscosity data and a density of $\rho = 9.1 \times 10^3$ kg/m³, the flotation velocity for gas bubbles in a PdNiCuP liquid as a function of temperature was calculated according to Stokes law. For simplicity, a constant bubble volume fraction of 30% was assumed. Three different bubble sizes of 5×10^{-3} m, 5×10^{-4} m, and 1×10^{-4} m have been considered. At a temperature of 900 K with a corresponding viscosity of 86 Pa s, a velocity of $V = 1 \times 10^{-3}$ m/s for bubbles of a radius of 5×10^{-3} m, $V = 4 \times 10^{-5}$ m/s for the 5×10^{-4} m bubble, and $V = 4 \times 10^{-7}$ m/s for the 1×10^{-4} m bubble was calculated. By comparing the time scale for flotation with the time scale of the experiment of 20 s, one can conclude that no noticeable gradient should be expected for bubbles of a radius of 5×10^{-4} m or less. The results suggest that the flotation velocity of gas bubbles in pure metals is three orders of magnitude higher owing to the three orders of magnitude lower

viscosity. Therefore, in liquid pure metals, even bubbles with a radius of 1×10^{-4} m show significant flotation on the time scale of the experiment.

In order to ensure that the foam can be vitrified upon cooling a thermal analysis measurement was performed by heating the prefoam and foam materials at a rate of 0.33 K/s. Both thermograms for the samples look very similar. For example, the thermogram for the prefoam sample indicated that the material's glass transition temperature is $T_g = 578$ K, the crystallization temperature is $T_x = 667$ K, and the heat of crystallization is $\Delta H = 3 \times 10^3$ J/mol. Solidus and liquidus temperatures are 804 K and 859 K, respectively. Meanwhile, for the foamed sample, $T_g = 577$ K, $T_x = 666.8$ K, and $\Delta H = 2.9 \times 10^3$ J/mol. Solidus and liquidus temperatures are 804 K and 858 K, respectively. The fact that T_g and T_x are not altered by the foaming process indicates that the foaming does not degrade the glass forming ability. A similar heat of crystallization measured for the two alloys proves that the foam is entirely amorphous.

EXAMPLE 2:

A low density amorphous PdNiCuP was made by mixing ingots of the PdNiCuP with hydrated B_2O_3 . The B_2O_3 releases gas at temperatures around the melting temperature of the alloy and creates a large number of small bubbles. The mixture of PdNiCuP and B_2O_3 is processed for 1200 s at 1200 K. The bubble containing liquid is then cooled with a rate that prevents detectable crystallization. The amorphous structure can be proven by differential scanning calorimetry (DSC).

The bubble volume fraction of the pre-cursor is between 10 and 20 % (see Figure 5a and Figure 5b). The amorphous pre-cursor was subsequently heated up in the supercooled liquid region to a temperature of 360 C and held there for 120 s. The pressure was decreased to about 10^{-3} mbar. During this time the pre-cursor expands. Figure 10 shows the resulting foam. The density is 2.2×10^3 kg/m³ compare to 9.1×10^3 kg/m³ of the bulk PdNiCuP sample. This results in a bubble volume fraction of about 75 %. DSC measurements on the foamed sample showed that no noticeable crystallization took place during the expansion process.

The preceding description has been presented with reference to presently preferred embodiments of the invention. Workers skilled in the art and technology to which this invention pertains will appreciate that alterations and changes in the described structures and processes may be practiced without meaningfully departing from the principal, spirit and scope of this invention.

Accordingly, the foregoing description should not be read as pertaining only to the precise structures described and illustrated in the accompanying drawings, but rather should be read consistent with and as support to the following claims which are to have their fullest and fair scope.

WHAT IS CLAIMED IS:

1. A method of making a metallic glass foam from a bulk-solidifying amorphous alloy as described herein.
2. An apparatus for making a metallic glass foam from a bulk-solidifying amorphous alloy as described herein.
3. A metallic glass foam article made from a bulk-solidifying amorphous alloy as described herein.

49622/JWP/L471

METHOD OF MANUFACTURING METALLIC FOAM FROM METALLIC GLASS FORMING LIQUIDS

ABSTRACT

An apparatus and method for controllably manufacturing metallic foams from high viscosity materials, and more particularly for controllably manufacturing metallic foams from metallic glass forming liquids are described.

Figure 1

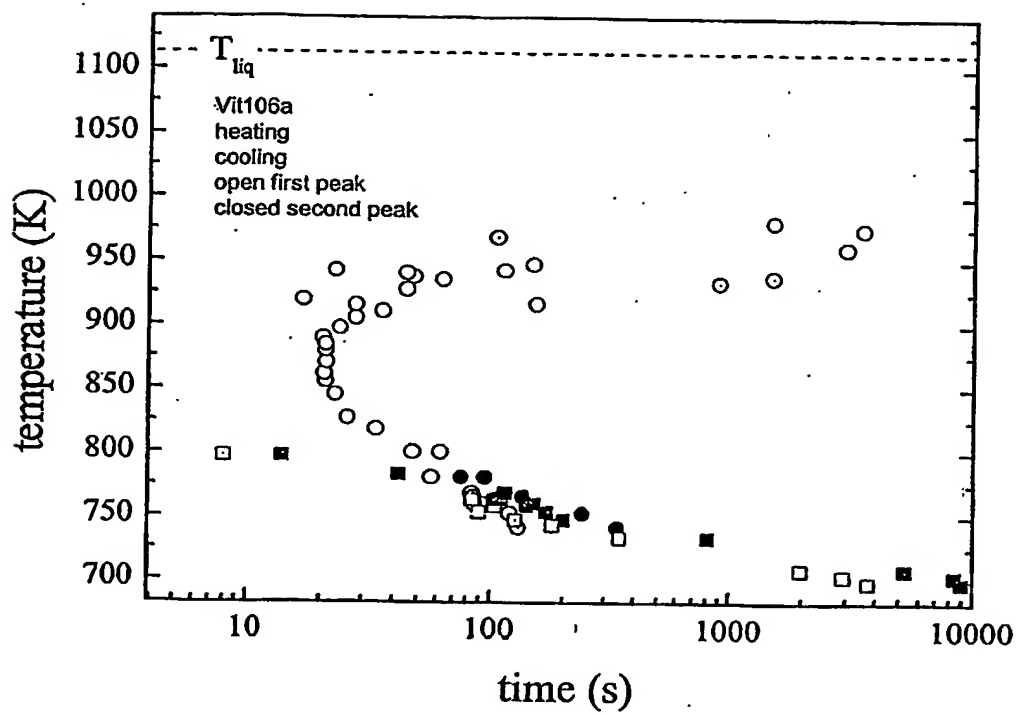


Figure 2

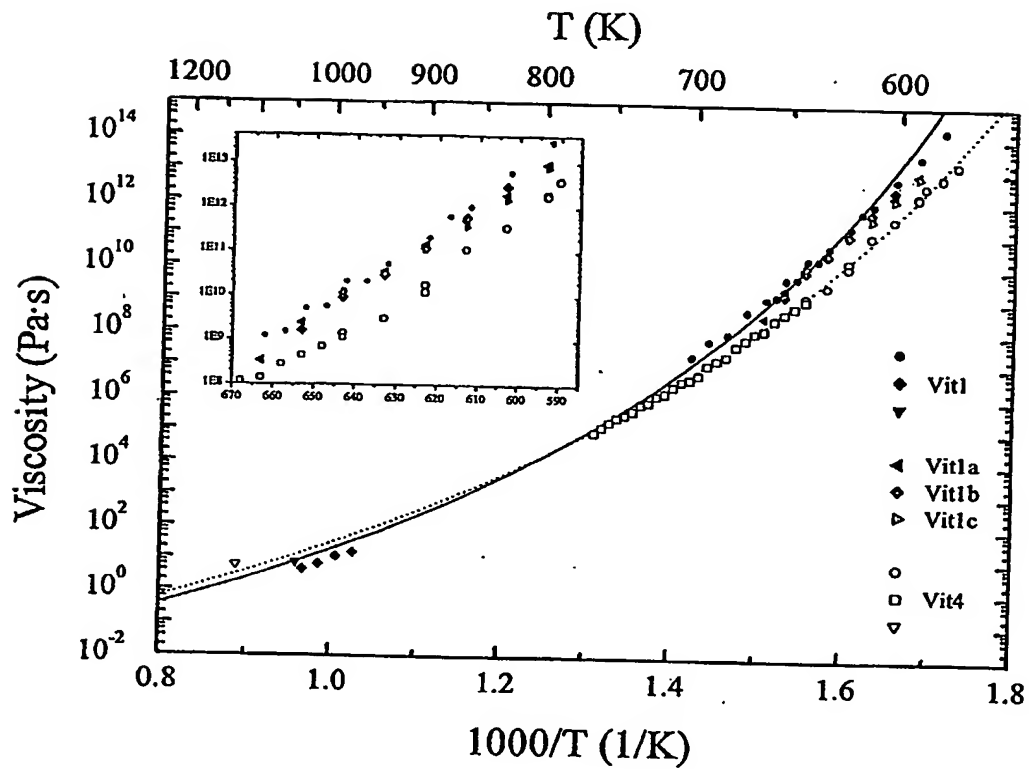


Figure 3

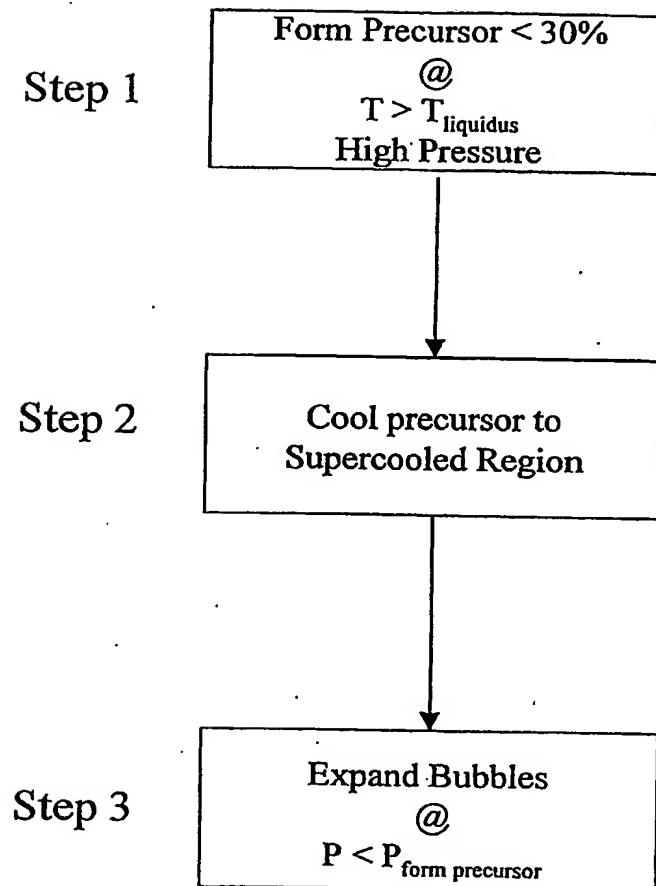


Figure 4a

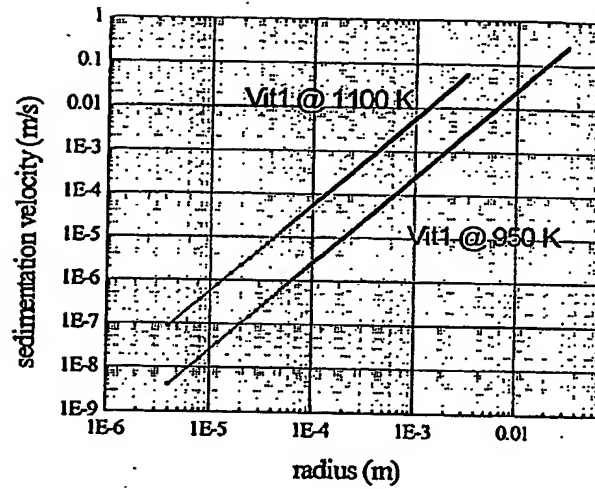


Figure 4b

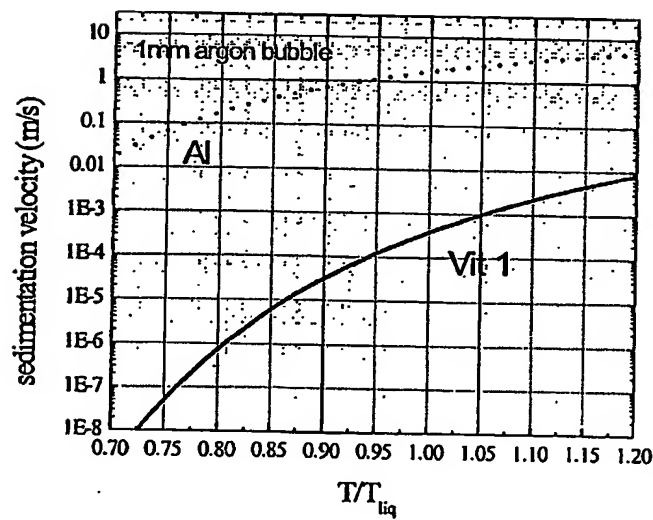


Figure 5a

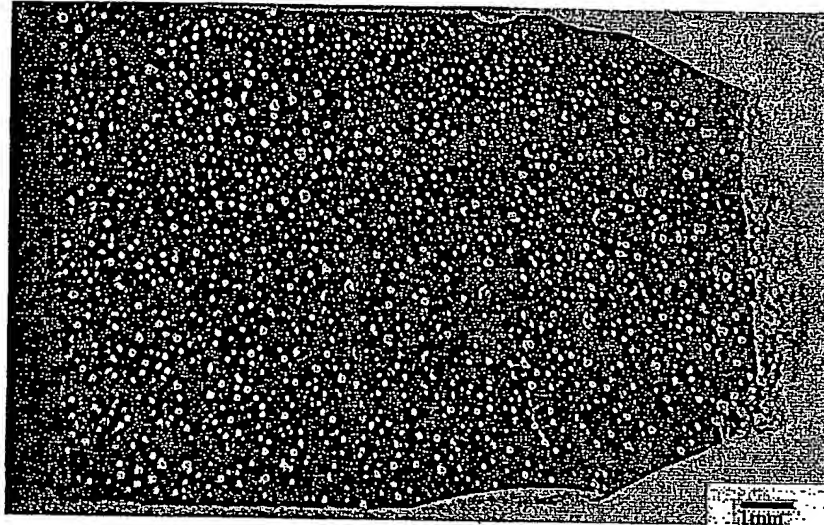


Figure 5b

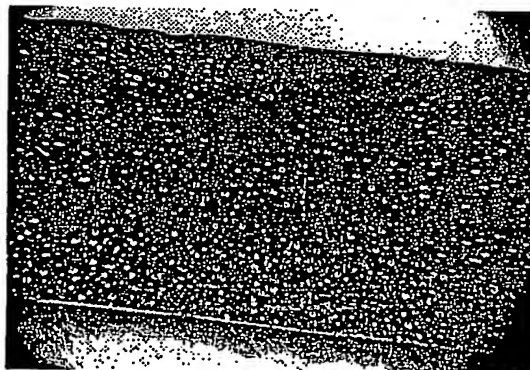


Figure 6

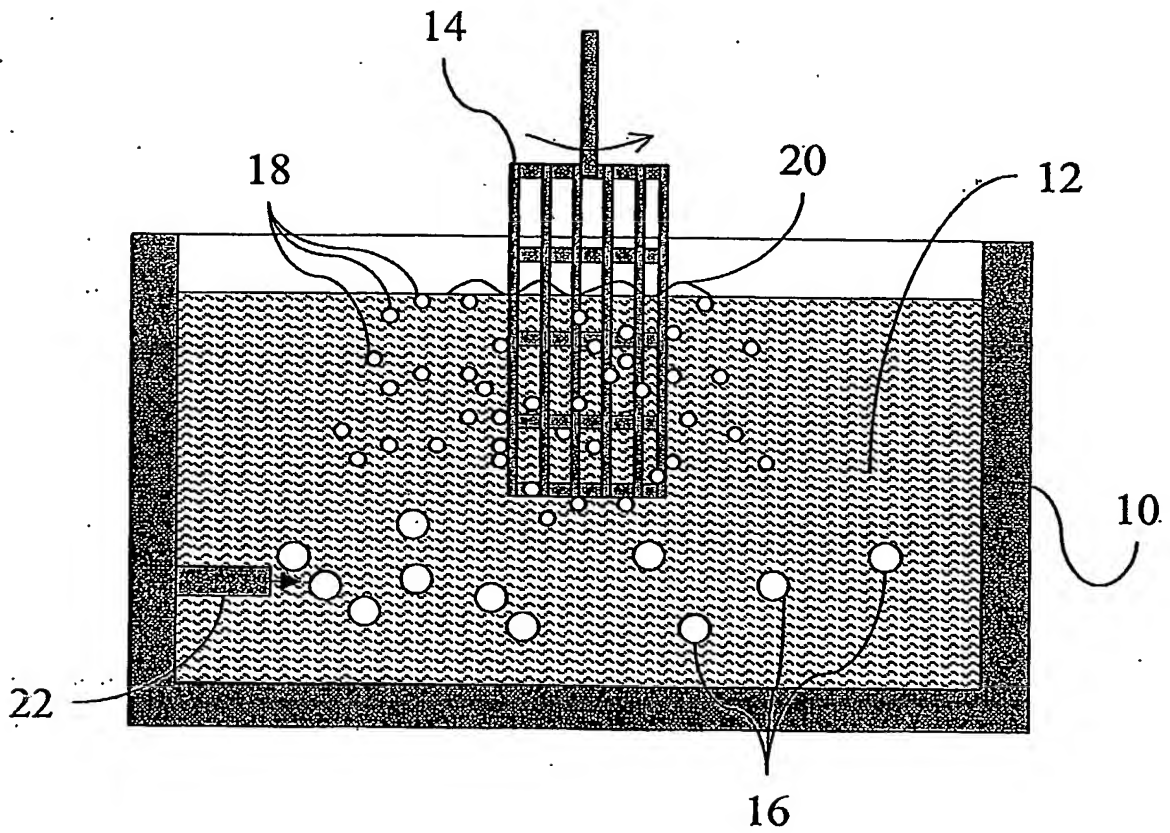


Figure 7

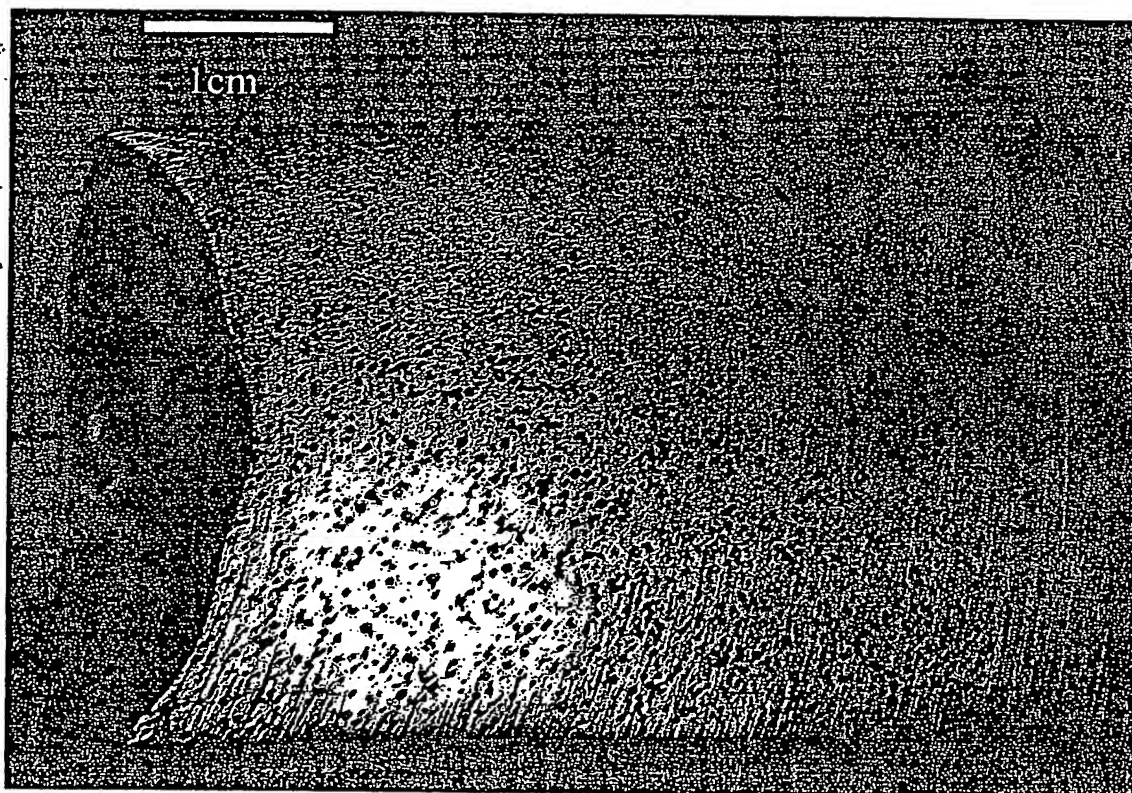


Figure 8

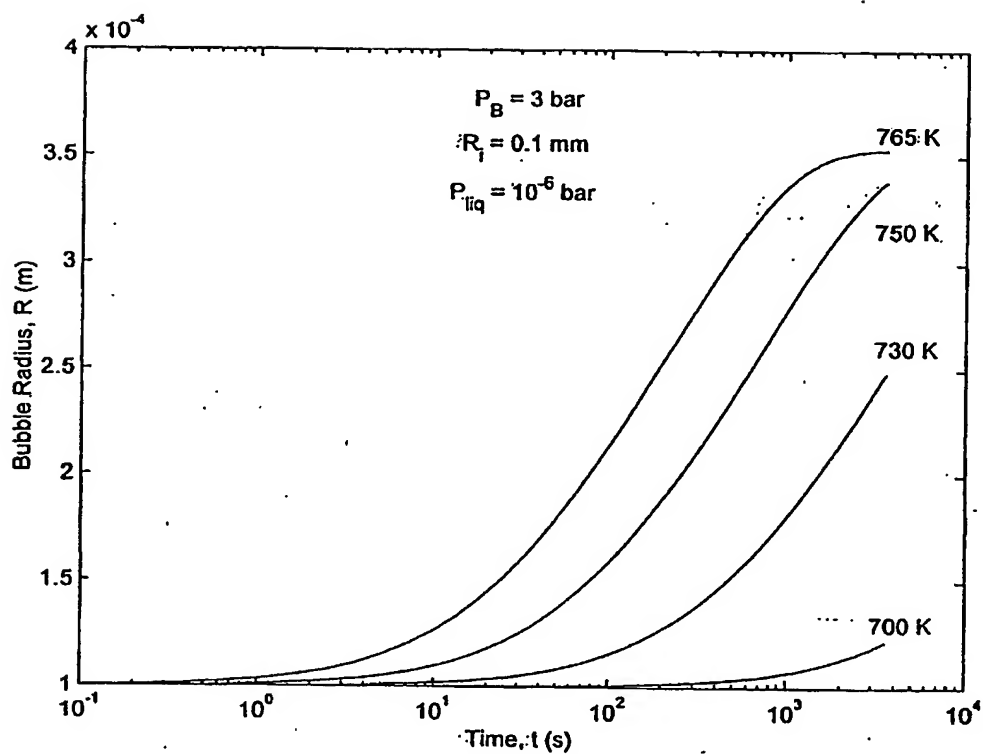


Figure 9

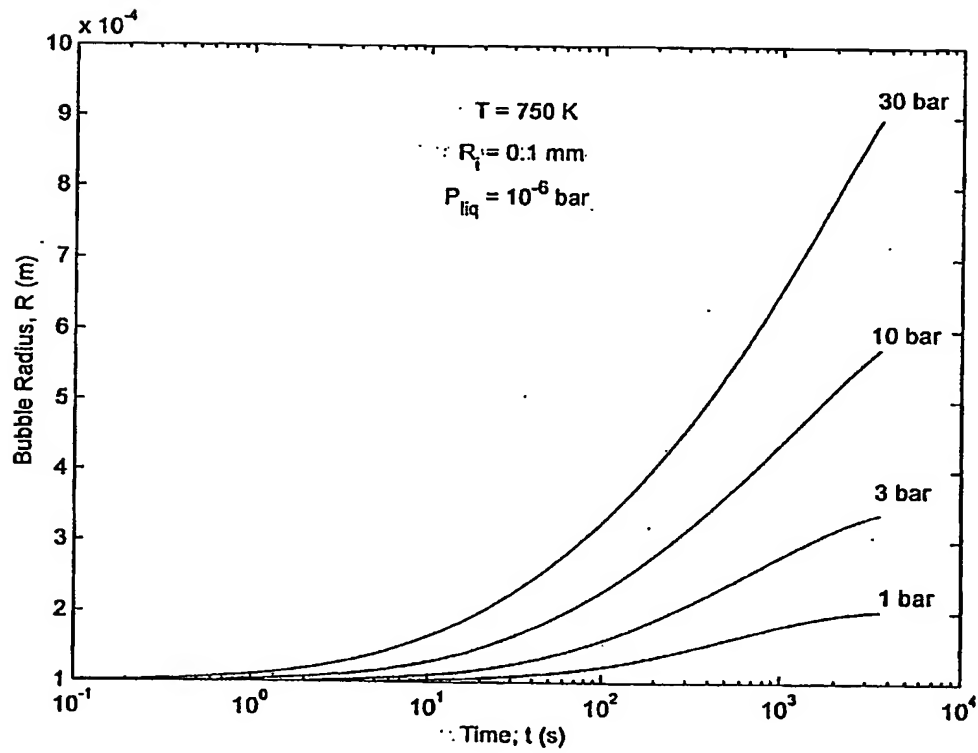


Figure 10

